

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
24 February 2005 (24.02.2005)

PCT

(10) International Publication Number
WO 2005/017215 A1

(51) International Patent Classification⁷: C22B 3/06, 11/00

(21) International Application Number:
PCT/AU2004/001104

(22) International Filing Date: 18 August 2004 (18.08.2004)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
2003904385 18 August 2003 (18.08.2003) AU

(71) Applicant (for all designated States except US): MURDOCH UNIVERSITY [AU/AU]; South Street, Murdoch, Western Australia 6150 (AU).

(72) Inventor; and

(75) Inventor/Applicant (for US only): ZHANG, Hongguang [AU/AU]; 137 Parry Avenue, Bull Creek, Western Australia 6149 (AU).

(74) Agent: WRAY & ASSOCIATES; Level 4, The Quadrant, 1 William Street, Perth, Western Australia 6000 (AU).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 2005/017215 A1

(54) Title: IMPROVED THIOSULPHATE LEACH PROCESS

(57) Abstract: An improved thiosulphate leach process for the recovery of gold from ores and other gold-bearing materials, characterised in that the leach solution comprises thiosulphate, thiourea or a reagent chemically related thereto, and an oxidant that does not oxidise thiosulphate, the process producing a pregnant leach solution from which gold may be recovered.

"Improved Thiosulphate Leach Process"

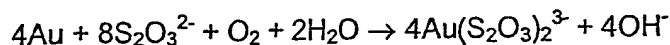
Field of the Invention

The present invention relates to an improved thiosulphate leach process. More particularly, the thiosulphate leach process of the present invention is intended for
5 use in the extraction of gold from ores or other gold-bearing materials using thiosulphate as a lixiviant in the absence of ammonia/ammonium and copper ions.

Background Art

The process of alkaline cyanidation for the extraction of gold from its ores has been practised for over a century and remains the predominant method world
10 wide in gold production. Despite its proven records, there have been increasing concerns in the community over the high toxicity of cyanide, which poses serious health and environmental risks. In fact, some countries have now banned the construction of new cyanidation plants. Under these circumstances, alternative non-toxic lixivants for the extraction of gold have been investigated, including the
15 use of a thiosulphate lixiviant.

In a thiosulphate solution containing an oxidant such as dissolved oxygen, gold may be dissolved as the gold-thiosulphate complex according to the following reaction:



20 Although the reaction is favoured thermodynamically, the rate at which gold dissolves is very slow unless a catalyst and a redox mediator are present. This is thought to be the result of: (i) Oxygen is not an effective oxidant because of its slow reduction on the gold surface. (ii) The dissolution of gold is hindered because of the passivation of the gold surface in the thiosulphate solution.

25 In order to obtain a reasonably fast leaching rate, it is generally understood that ammonia and copper ions are required in the thiosulphate solution under alkaline

- 2 -

conditions (e.g. pH > 9). Ammonia, usually added as the ammonium thiosulphate salt, helps stabilise the copper as the copper(II) tetrammine complex which serves as an effective oxidant. The copper(II) tetrammine is regenerated by oxidation of the copper(I) complex by dissolved oxygen. In addition, it has been shown that

5 both ammonia and copper may have catalytic effect on the anodic half reaction of gold oxidation. This process is described in, for example, US Patent 4269622 (Kerley, Jr.), US Patent 4369061 (Kerley Jr.) and US Patent 4654078 (Perez et al.).

There are several substantial drawbacks associated with the ammonia- copper-thiosulphate leaching process. Firstly, copper is known to catalyse the oxidation of thiosulphate. This not only results in very high reagent consumption, but also generates significant amounts of polythionates which may be detrimental to the down-stream gold recovery process. Secondly, the process is not robust, with the leaching conditions having to be controlled very carefully and often ore-specifically. Thirdly, concerns have been raised over the widespread use of ammonia in fairly large concentrations, which may be a potential hazard to the environment. For these reasons, no commercial applications of the ammonia-copper-thiosulphate process have yet been implemented.

10
15

The present invention has as one object thereof to overcome substantially the above problems associated with the prior art, or to at least provide a useful alternative thereto.

20

The preceding discussion of the background art is intended to facilitate an understanding of the present invention only. It should be appreciated that the discussion is not an acknowledgement or admission that any of the material referred to was part of the common general knowledge in Australia as at the priority date of the application.

25

Throughout the specification, unless the context requires otherwise, the word "comprise" or variations, such as "comprises" or "comprising", will be understood to imply the inclusion of a stated integer or group of integers but not the exclusion of any other integer or group of integers.

30

Disclosure of the Invention

In accordance with the present invention there is provided an improved thiosulphate leach process, the process characterised by the method steps of submitting a gold-bearing material to a leach in a thiosulphate solution, wherein
5 thiourea or a reagent chemically related thereto, and at least one oxidant, are present in the thiosulphate leach solution, and subsequently recovering gold from the resulting pregnant leach solution.

Preferably, thiourea is provided in a concentration of about 0.01 mole/L.

Preferably, the oxidant present is a complex of ethylenediaminetetraacetate
10 (EDTA) with a multivalent metal. The multivalent metal may be iron and the complex FeEDTA.

Still preferably, thiosulphate is added in the form of a soluble salt. In one form of the present invention the soluble salt is the sodium or ammonium salt of thiosulphate.

15 In one form of the present invention thiosulphate is provided in a concentration of about 0.1 to 0.3 mole/L.

The preferred oxidant FeEDTA may be prepared prior to addition to the leach solution or it may be prepared by adding suitable amounts of iron salts and EDTA directly to the leach solution.

20 Preferably, the concentration of FeEDTA in the leach solution is about 0.002 mole/L.

The pH of the leach is preferably maintained between about 6 to 7.

The reagent chemically related to thiourea may preferably include one or more thio-substituted organic compounds, including but not limited to formamidine
25 disulphide and thiosemicarbazide.

In accordance with the present invention there is further provided an improved thiosulphate leach process for the recovery of gold from ores and other gold-bearing materials, characterised in that the leach solution comprises thiosulphate, thiourea or a reagent chemically related thereto, and an oxidant that does not
5 oxidise thiosulphate, the process producing a pregnant leach solution from which gold may be recovered.

Preferably, the oxidant present is a complex of ethylenediaminetetraacetate (EDTA) with a multivalent metal. The multivalent metal may be iron and the complex FeEDTA.

10 The FeEDTA may be provided at a concentration of about 0.002 mole/L.

Still preferably, the thiosulphate is provided at a concentration of 0.1 to 0.3 mole/L. Further, thiourea is preferably provided at a concentration of 0.01 mole/L.

In one form of the present invention, gold is recovered from the pregnant leach solution by way of either cementation or ion exchange.

15 The pH of the leach is preferably maintained between about 6 to 7.

The reagent chemically related to thiourea may preferably include one or more thio-substituted organic compounds, including but not limited to formamidine disulphide and thiosemicarbazide.

Best Mode(s) for Carrying Out the Invention

20 In one embodiment of the process of the present invention, that process involves the leaching of gold using a solution containing thiosulphate, thiourea and an effective oxidant. The oxidant is provided in the form of an EDTA complex with a multivalent metal, for example iron, which provides the complex FeEDTA. Thiosulphate can be added as the sodium salt or any other soluble salt of
25 thiosulphate. The preferred concentration of thiosulphate is 0.1 – 0.3 mole/L, but lower or higher concentrations in the range of 0.02 to 1 mole/L may also be used.

The role of thiourea is to catalyse the half reaction of gold oxidation. The preferred concentration of thiourea is 0.01 mole/L though higher or lower concentrations are also applicable, in the range of 0.002 to 0.1 mole/L.

5 The inventor has determined that reagents chemically related to thiourea have the same impact on the process of the present invention as does thiourea. These chemically related reagents are understood to include other thio-substituted organic compounds, including but not limited to formamidine disulfide ($\text{NH}_2(\text{NH})\text{CSSC}(\text{NH})\text{NH}_2$) and thiosemicarbazide ($\text{SC}(\text{NH}_2)\text{NHNH}_2$).

10 An oxidant is essential for the leaching of gold and one of the least expensive oxidants is dissolved oxygen. However, oxygen alone is not sufficient to extract gold effectively in such a system. A practical thiosulphate leaching system requires an oxidant that:

1. Has a reduction potential in excess of about 0.2 V;
2. Does not oxidise thiosulphate;
- 15 3. Can be preferably rapidly re-oxidised by oxygen; and
4. Is not too expensive.

The applicant has determined that FeEDTA is such an oxidant. The oxidant can be prepared prior to leaching by mixing a ferric salt, such as ferric nitrate or ferric sulphate, in a solution with EDTA. Alternatively, it can be prepared using a
20 ferrous salt in the presence of dissolved oxygen using the same procedure. The ferrous EDTA complex formed is then oxidised to FeEDTA by the dissolved oxygen. It is also possible to prepare the FeEDTA by adding suitable amounts of iron salts and EDTA directly to the leaching slurry where the complex is formed *in-situ*. The concentration of the FeEDTA may be as low as about 0.001 mole/L, but
25 is preferably about 0.002 mole/L, to minimise the cost. It is envisaged that higher concentrations, up to about 0.01 mole/L, may result in better kinetics and gold recoveries.

Ideally, the leach is carried out in neutral pH and at ambient temperature (understood to mean between about 20-30°C) and over a period of up to 48 to 72 hours. The leach may be conducted at elevated temperatures, although gold recovery may be inversely affected by the increase in temperature. Temperatures of up to about 50°C are envisaged for ores, whilst higher temperatures may be employed with concentrates.

The process described is simple and provides leaching kinetics comparable to known cyanidation processes. Another important advantage is that the FeEDTA oxidant oxidises only gold and not thiosulphate. As a result, the reagent consumption is low in contrast to the relatively heavy loss of thiosulphate associated with the prior art ammonia-copper-thiosulphate leaching process. After leaching, the gold in the pregnant solution can be recovered using those techniques proposed for the ammonia-copper-thiosulphate process, such as cementation or ion exchange.

The improved thiosulphate leach process of the present invention will now be described with reference to several non-limiting examples:

EXAMPLE 1

Gold powder prepared by reduction precipitation from a AuCl_4^- solution was leached using an oxygenated sodium thiosulphate solution (0.1 mole/L) containing thiourea (0.01 M) at pH 6 and ambient temperature. The leach was run for 96 hours in a stirred reactor with 19.4 ppm gold dissolved (69.3% recovery). For comparison, only 3.6 ppm gold was dissolved (18.4% recovery) under the same conditions but in the absence of thiourea. This example indicates that the addition of thiourea catalyses the oxidation of gold and that oxygen alone is understood to be insufficient for satisfactory leaching kinetics for practicable gold plant operation (typically 24 to 48 hours maximum leach times) and gold adequate recovery.

EXAMPLE 2

An ore sample (Ore 1) obtained from a cyclone overflow was used for the leaching tests using the improved process of the present invention, at a grind size of 75% passing 75 μm . This ore contains about 2 g/t gold in average. The leaching conditions are outlined below:

Sodium thiosulphate concentration: 0.3 mole/L

Thiourea concentration: 0.01 mole/L initially and extra 0.01 mole/L was added after 8 hours

10 FeEDTA concentration: 0.003 mole/L initially and extra 0.002 mole/L was added after 8 hours

Slurry pulp density: 40% (wt.)

pH range: 6.5 – 8

Temperature: Ambient

Leaching time: 24 hours

15 The gold recovery was 88-90%.

EXAMPLE 3

An ore sample (Ore 1) collected from cyclone underflow, was ground and screened and the portion with particle sizes of $-150 \mu\text{m}$ was used for the leaching tests. The average grade of gold is about 17.4 g/t. The leaching conditions were:

20 Sodium thiosulphate concentration: 0.3 mole/L

Thiourea concentration: 0.01 mole/L initially and extra 0.01 mole/L was added after 8 hours

FeEDTA concentration: 0.003 mole/L initially and extra 0.002 mole/L was added after 8 hours

25 Slurry pulp density: 40% (wt.)

- 8 -

pH range: 6.5 – 8
Temperature: Ambient
Leaching time: 24 hours

5 Gold recoveries of 92.5-97.5% were achieved using the above specified leaching conditions.

EXAMPLE 4

An ore sample (Ore 2) was obtained containing 2.5 g/t gold, sized as 100% passing 150 μ m. The thiosulphate leaching tests were performed under the following conditions:

10 Sodium thiosulphate concentration: 0.3 mole/L
Thiourea concentration: 0.01 mole/L
FeEDTA concentration: 0.003 mole/L
Slurry pulp density: 40% (wt.)
pH range: 6.5 – 8.5
15 Temperature: ambient
Leaching time: 24 hours

The recovered values of gold after leaching under such conditions are typically 89.6-98%.

20 Examples 1 to 4 described the technical details of the improved thiosulfate leaching process and provide details for the leaching of pure gold powder (Example 1) and ore (Examples 2 to 4), with the ore samples prepared by dry grinding. Further tests were carried out using another ore which was prepared using both dry and wet grinding methods. The leaching of dry ground (ring milled)

samples yielded similar results to those obtained from the ores of Examples 2 to 4, with gold recoveries of around 90% achieved.

EXAMPLE 5

An ore sample containing 2.5-5 g/t gold was crushed and then ground in a ring mill to a P_{100} of -150 μm . The leaching was conducted in rolling bottles or in stirred tank reactors under the conditions summarised below:

	Sodium thiosulfate concentration:	0.3 mole/L
	Thiourea concentration:	0.01 mole/L
	FeEDTA concentration:	0.003 mole/L
10	Pulp density:	40% (wt.)
	pH range:	6.5-8.5
	Temperature:	ambient (20-25°C)
	Leaching time:	24 hours

Gold recoveries obtained under the above conditions were typically 83-91%.

15 The wet ground (rod milled) samples may be contaminated with metallic iron. If this happens, direct leaching of the ore after grinding may not be successful because the metallic iron consumes the FeEDTA oxidant. However, this problem can be solved by pre-aeration of the slurry for a few hours to oxidise the metallic iron, or by magnetic separation to remove the metallic iron. After the removal of
20 the metallic iron gold leaching can be proceeded under similar conditions described in the previous examples.

The Examples 1 to 5 were conducted without particular control of pH. The initial pH was about 6.5 which increased gradually to above 8 upon contact with the ores. However, it has now been found that the reduction of the FeEDTA oxidant
25 becomes less effective at pH values above about 7. This can result in significant

decreases in gold leaching rate and, consequently, gold recovery. A solution to this problem is to carry out the leaching with the pH controlled below about 7, as demonstrated by the following Example.

EXAMPLE 6

- 5 An ore sample containing 2.5-5 g/t gold, was crushed and then ground in a rod mill at 50% solids to 99.6% -150 μm . The ore was contaminated by metallic iron during the grinding. The metallic iron was then removed either by magnetic separation or by pre-aeration of the slurry for 24 hours before the reagents were added. The leaching was conducted in stirred tank reactors and the pH of the
- 10 slurry was controlled between 6 and 7 throughout the leach. This was done either by addition of dilute sulphuric acid during the leaching, or by using a buffer solution containing 0.25 mole/L KH_2PO_4 and a suitable concentration of NaOH to adjust the pH to 6-7. Other leaching conditions are specified below:

Sodium thiosulfate concentration: 0.3 mole/L

15 Thiourea concentration: 0.01 mole/L

FeEDTA concentration: 0.003 mole/L

Pulp density: 40% (wt.)

Temperature: ambient (23-28°C)

Leaching time: 24 hours

- 20 Under the above specified conditions, the gold recovered was typically 87-92%.

Modifications and variations such as would be apparent to a skilled addressee are considered to fall within the scope of the present invention.

Claims

1. An improved thiosulphate leach process, the process characterised by the method steps of submitting a gold-bearing material to a leach in a thiosulphate solution, wherein thiourea or a reagent chemically related thereto, and at least one oxidant, are present in the thiosulphate leach solution, and subsequently recovering gold from the resulting pregnant leach solution.
2. A process according to claim 1, wherein thiourea is provided in a concentration of about 0.01 mole/L.
3. A process according to claim 1 or 2, wherein the oxidant present is a complex of ethylenediaminetetraacetate (EDTA) with a multivalent metal.
4. A process according to claim 3, wherein the multivalent metal is iron and the complex FeEDTA.
5. A process according to any one of the preceding claims, wherein thiosulphate is added in the form of a soluble salt.
6. A process according to claim 5, wherein the soluble salt is the sodium salt of thiosulphate.
7. A process according to any one of the preceding claims, wherein thiosulphate is provided in a concentration of about 0.1 to 0.3 mole/L.
8. A process according to any one of claims 4 to 7, wherein the oxidant FeEDTA is prepared prior to addition to the leach solution.
9. A process according to any one of claims 4 to 7, wherein the oxidant FeEDTA is prepared by adding suitable amounts of iron salts and EDTA directly to the leach solution.

10. A process according to any one of claims 4 to 9, wherein the concentration of FeEDTA in the leach solution is about 0.002 mole/L.
11. A process according to any one of the preceding claims, wherein the pH of the leach is preferably maintained between about 6 to 7.
- 5 12. A process according to any one of the preceding claims, wherein the reagent chemically related to thiourea is a thio-substituted organic compound.
13. A process according to claim 12, wherein the reagent chemically related to thiourea is one of formamidine disulphide or thiosemicarbazide.
14. An improved thiosulphate leach process for the recovery of gold from ores
10 and other gold-bearing materials, characterised in that the leach solution comprises thiosulphate, thiourea or a reagent chemically related thereto, and an oxidant that does not oxidise thiosulphate, the process producing a pregnant leach solution from which gold may be recovered.
- 15 15. A process according to claim 14, wherein the oxidant present is a complex of ethylenediaminetetraacetate (EDTA) with a multivalent metal.
16. A process according to claim 15, wherein the multivalent metal is iron and the complex FeEDTA.
17. A process according to any one of claims 14 to 16, wherein the FeEDTA is provided at a concentration of about 0.002 mole/L.
- 20 18. A process according to any one of claims 14 to 17, wherein the thiosulphate is provided at a concentration of between about 0.1 to 0.3 mole/L.
19. A process according to any one of claims 14 to 17, wherein thiourea is provided at a concentration of about 0.01 mole/L.

- 13 -

20. A process according to any one of claims 14 to 18, wherein gold is recovered from the pregnant leach solution by way of either cementation or ion exchange.
21. A process according to any one of claims 14 to 19, wherein the pH of the leach is preferably maintained between about 6 to 7.
22. A process according to any one claims 12 to 21, wherein the reagent chemically related to thiourea is a thio-substituted organic compound.
23. A process according to claim 22, wherein the reagent chemically related to thiourea is one of formamidine disulphide or thiosemicarbazide.
24. An improved thiosulphate leach process substantially as hereinbefore described with reference to Examples 2 to 6.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU2004/001104

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl. ⁷: C22B 3/06, 11/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC⁷: C22B 3/00, 3/04, 3/00, 11/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Derwent WPI: IPC⁷ as above and thiosul+ and thiourea and EDTA

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5260040 A (Kenna) 9 November 1993 Whole Document	
A	US 6602319 B1 (Murthy et al) 5 August 2003 Whole Document	
A	US 6344068 B1 (Fleming et al) 5 February 2002 Whole Document	

☐ Further documents are listed in the continuation of Box C ☒ See patent family annex

* Special categories of cited documents:	
"A" document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E" earlier application or patent but published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search 2 September 2004	Date of mailing of the international search report 15 SEP 2004
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaustalia.gov.au Facsimile No. (02) 6285 3929	Authorized officer DAVID K. BELL Telephone No : (02) 6283 2309

INTERNATIONAL SEARCH REPORT

information on patent family members

International application No.

PCT/AU2004/001104

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member			
US 5260040		AU 73031/91	BR 9104641	CA 2047711	
		CN 1054268	EP 0476078	GB 2248632	
		NZ 237011	WO 9113177	ZA 9100943	
US 6602319					
US 6344068		AU 31355/01	CA 2342692	ZA 200102563	
Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.					
END OF ANNEX					